

ASPHERICITY AND PROLATENESS OF LINEAR AND CIRCULAR MACROMOLECULES*

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ABSTRACT

The shape asymmetry of gaussian models of linear and circular macromolecules has been numerically investigated in terms of asphericity and prolateness parameters. These parameters are found to decrease with increasing length for the macromolecule either confined to a plane or in three dimensions. The effect of dimensionality on these parameters is visible only for low dimensions and is generally weak. As dimensionality goes to infinity, it is found that asphericity and prolateness for both chains and rings approach slowly yet descendingly values of corresponding asphericity and prolateness factors, with the exception of the chain which shows a minimum value of asphericity when the embedding space has a dimensionality of four.

INTRODUCTION

In the framework of gaussian model, a macromolecule is pictured as a molecular graph^[1,2]: n vertices or beads connected in a definite way by a certain number of edges or segments. Thus a linear macromolecule is a chain of n beads connected consecutively by $n-1$ segments while a circular one a ring of n beads by n segments. Theoretical investigation on shapes of these simplest chains has been going on for more than six decades, with much emphasis on numerical evaluations of their shape distributions^[3-14]. More recently, however, there have appeared new measures that try to characterize shape asymmetry of a macromolecule in the approximation of both gaussian and Edwards model^[15], i. e., asphericity and prolateness

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(factors and parameters)^[16-25].

This paper is intended to complete the study of asphericity and prolateness of gaussian chains and rings based on a general formalism for calculating these quantities, the details of which are to be published elsewhere. In what follows, some formulas for their numerical computations are first presented, numerical results then follow, and finally a discussion and some conclusions are given.

THEORY

Let λ be the arithmetic mean of the radius of gyration of a chain or ring and Δ the gyration tensor minus a unit matrix multiplied by λ . Denoting by d dimensionality of space in which the chain or ring is embedded, we write $A = \text{Tr}(\Delta)^2 / [d(d-1)\lambda^2]$ and $P = \text{Tr}(\Delta^3) / [d(d-1)(d-2)\lambda^3]$, and call ensemble averages of A and P , i. e., $\langle A \rangle$ and $\langle P \rangle$, asphericity (parameter) and prolateness (parameter), respectively. We further define asphericity factor δ as $\langle \text{Tr}(\Delta^2) \rangle / \langle d(d-1)\lambda^2 \rangle$ and prolateness factor ζ as $\langle \text{Tr}(\Delta^3) \rangle / \langle d(d-1)(d-2)\lambda^3 \rangle$, for which there exist complete analytic expressions^[13,14] especially in the cases of chains and rings. We note that both $\langle A \rangle$ and δ fall within the interval $[0, 1]$ while $\langle P \rangle$ and ζ the interval $[-(d-1)^{-3}, 1]$, with the value of 0 corresponding to spherical symmetry and 1 to rodlike asymmetry or the highest degree of prolateness, and the interval $[-(d-1)^{-3}, 0)$ to the oblate region for all these measures^[7,16-19].

By use of the Diehl and Eisenriegler technique^[21], i. e., the integral and Gamma function representation of the factors $1/\lambda^m$ ($m = 2, 3$) in the definitions of A and P , and the Solc-Wei-Eichinger method^[5,13], we find that for finite- n chains,

$$\langle A \rangle = 2^{-1} \alpha_1(d) \int_0^\infty \text{sh}^{-1} x \text{ch}^{-2}(x/2) F_n(x) [g_n(x)]^{d/2+2} dx \quad (1)$$

and

$$\langle P \rangle = 2^{-2} \alpha_2(d) \int_0^\infty \text{sh}^{-1} x \text{ch}^{-4}(x/2) G_n(x) [g_n(x)]^{d/2+3} dx \quad (2)$$

and that for finite- n rings,

$$\langle A \rangle = \alpha_1(d) \int_0^\infty \text{sh}^{-1} x \text{ch}^{-3}(x/2) M_n(x) [g_n(x/2)]^{d-1} dx \quad (3)$$

and

$$\langle P \rangle = \alpha_2(d) \int_0^\infty \text{sh}^{-1} x \text{ch}^{-5}(x/2) N_n(x) [g_n(x/2)]^{d-1} dx \quad (4)$$

where $M_n(x)$ and $N_n(x)$ are defined as

$$M_n(x) = g_n(x/2) \text{sh } x \text{sh}^3(x/2) + F_{n/2}(x) [g_{n/2}(x)]^3 \quad (5)$$

and

$$N_n(x) = g_n(x/2) \operatorname{sh} x \operatorname{sh}^5(x/2) + G_{n/2}(x) \operatorname{ch}(nx/2) [g_{n/2}(x)]^4 \quad (6)$$

respectively, $F_n(x)$ and $G_n(x)$ as

$$F_n(x) = 1 + \operatorname{ch} x [g_{2n}(x)]^{-1} - [1 + \operatorname{ch}^2 x] [g_n(x)]^2 \quad (7)$$

and

$$G_n(x) = 1 + [1 + 2^{-1} \operatorname{ch}(2x)] [g_n(x)]^2 + \operatorname{ch} x w_n(x) [g_n(x)]^{-1} \quad (8)$$

respectively, and $w_n(x)$ is given by

$$w_n(x) = \{3/2 - (3 + \operatorname{ch}^2 x) [g_n(x)]^{-2}\} / \operatorname{ch}(nx) \quad (9)$$

while $g_n(x) = n \operatorname{sh} x / \operatorname{sh}(nx)$, $\alpha_1(d) = d(1 + d/2)/2$, and $\alpha_2(d) = \alpha_1(d)(1 + d/4)$.

For infinitely long chains and rings which correspond to open and closed random walks, respectively, we find that

$$\langle A \rangle = 2^{-1} \alpha_1(d) \int_0^\infty F(x) [\alpha(x)]^{d/2} x^{-1} dx \quad (10)$$

and

$$\langle P \rangle = 2^{-3} \alpha_2(d) \int_0^\infty G(x) [\alpha(x)]^{d/2} x^{-1} dx \quad (11)$$

for chains and

$$\langle A \rangle = \alpha_1(d) \int_0^\infty F(x) \alpha^d(x) x^{-1} dx \quad (12)$$

and

$$\langle P \rangle = 2^{-2} \alpha_2(d) \int_0^\infty G(x) \alpha^d(x) x^{-1} dx \quad (13)$$

for rings, where $\alpha(x) = x / \operatorname{sh} x$, and $F(x)$ and $G(x)$ are defined as

$$F(x) = \alpha(x) \operatorname{ch} x + \alpha^2(x) - 2 \quad (14)$$

and

$$G(x) = \alpha(x) [3 + 2\alpha^2(x)] \operatorname{ch} x + 3\alpha^2(x) - 8 \quad (15)$$

respectively. We note that for $d = 2$ eq. 12 reduces to that first given by Levinson^[23] and eqs. 10–13 can be further simplified with the results expressed in terms of the simpler integral

$$M(d) = \int_0^\infty x \alpha^d(x) dx \quad (16)$$

as first done for $\langle A \rangle$ by Diehl and Eisenriegler^[21]. These and other results such as the so called $1/d$ -expansions of $\langle A \rangle$ and $\langle P \rangle$ for large d will be presented elsewhere.

NUMERICAL RESULTS

With the use of Mathematica[®] the integrals in eqs. 1–4 and 10–13

Table 1 Length-dependence of asphericity for 2D chains and rings

n	chain		ring	
	$\langle A \rangle$	δ	$\langle A \rangle$	δ
03	0.701463	0.769231	0.666667	0.666667
04	0.580468	0.684211	0.514043	0.529412
05	0.518060	0.644068	0.432715	0.461538
06	0.482493	0.622047	0.384753	0.423423
12	0.418687	0.584158	0.295142	0.356322
99	0.396732	0.571616	0.263043	0.333673
∞	0.396400	0.571429	0.262553	0.333333

Table 2 Length-dependence of asphericity for 3D chains and rings

n	chain		ring	
	$\langle A \rangle$	δ	$\langle A \rangle$	δ
04	0.556588	0.643564	0.471722	0.483871
05	0.499250	0.601266	0.394971	0.416667
06	0.467611	0.578331	0.351387	0.379645
07	0.448355	0.564516	0.324383	0.357143
12	0.412806	0.539305	0.273487	0.315682
99	0.394547	0.526507	0.246771	0.294435
∞	0.394274	0.526316	0.246368	0.294118

Table 3 Length-dependence of prolateness for 3D chains and rings

n	chain		ring	
	$\langle P \rangle$	ζ	$\langle P \rangle$	ζ
04	0.375950	0.547083	0.265493	0.287301
05	0.319698	0.506927	0.195969	0.230263
06	0.291889	0.486492	0.162278	0.203181
07	0.276183	0.474646	0.143730	0.188291
12	0.249797	0.453941	0.114099	0.164073
99	0.237649	0.443888	0.101601	0.153325
∞	0.237475	0.443740	0.101430	0.153173

Table 4 Dimensionality-dependence of asphericity and prolateness for infinitely long chains and rings

d	chain		ring	
	$\langle A \rangle$	$\langle P \rangle$	$\langle A \rangle$	$\langle P \rangle$
04	0.393829	0.234573	0.236900	0.092251
05	0.393919	0.232898	0.230665	0.086244
06	0.394189	0.231841	0.226240	0.082000
07	0.394510	0.231129	0.222936	0.078841
99	0.399335	0.228590	0.201829	0.058858
∞	0.400000	0.228571	0.200000	0.057143

may be accurately evaluated to give numerical values of $\langle A \rangle$ and $\langle P \rangle$ for

chains and rings both of any length and in an arbitrary d -dimensional space. We have made such calculations for selected values of n and d for both types of macromolecules.

The results showing the dependence of $\langle A \rangle$ and $\langle P \rangle$ on length of a chain or ring in both two and three dimensions are tabulated in Tables 1–3, while those indicating the effect of dimensionality on values of $\langle A \rangle$ and $\langle P \rangle$ for infinitely long chains and rings are in Table 4. The results based on existing analytic expressions^[13,14] for σ and ζ are also included in these Tables for comparison.

DISCUSSION AND CONCLUSION

From Tables 1–3, it is found that in either two or three dimensions, both asphericity (factor) and prolateness (factor) decrease as length of a chain or ring increases, approaching slowly their respective limiting values after a relatively large initial drop, and that numerical values of asphericity or prolateness factor are uniformly larger than those of the corresponding asphericity or prolateness parameter except for the 2D 3-bead ring which has its asphericity equal to its asphericity factor. It is also seen that a chain or ring in three dimensions has a lower value of asphericity than in two dimensions, and that a chain has a larger value of each of the four quantities than a ring of the same number of beads, implying higher shape asymmetry in the chain than in the ring, though they both show marked asphericity and a large degree of prolateness.

For infinitely long chains and rings, we find from Table 4 that asphericity of a chain shows a minimum when dimensionality approaches 4—the critical dimension for the disappearance of the excluded volume effect in the chain, while that of a ring exhibits monotonous decrease as dimensionality increases, as does prolateness for both chains and rings. We notice that as dimensionality goes to infinity, $\langle A \rangle$ approaches to δ and $\langle P \rangle$ approaches to ζ for both chains and rings, which is in agreement with the $1/d$ —expansion result^[20,21]. It is also worth noting that in three dimensions an Edwards chain (ring), i. e., an open (closed) random walk with self avoidance, has a slightly higher value of asphericity or prolateness as shown by Jagodzinski, Eisenriegler and Kremer^[24] with the use of the ϵ -expansion technique and Monte Carlo method, that is, a value of 0.416 (0.260) for asphericity (the ϵ —expansion result) and a value of 0.271 (0.103) for prolateness (the Monte Carlo result) as compared to that of

0.394274(0.246368) and that of 0.237475 (0.101430), respectively, thus implying on the average an slightly more extended shape resulted from the excluded volume effect for both chains and rings.

In conclusion, the length- and dimensionality-dependences of asphericity and prolateness of linear and circular macromolecules in the framework of gaussian model have been numerically thoroughly investigated. It is found that the increase in length reduces asphericity and prolateness for both chains and rings, while the increase in dimensionality results in the decrease of both asphericity and prolateness only for rings, and for chains, of prolateness only as asphericity shows a minimum when the chain is embedded in a 4-dimension space.

Keywords:

Asphericity; Prolateness; Macromolecular shape theory

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